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THE ORIGIN OF BOMBSHELL ORE.

By H. M. CHANCE.

(Read May 15, 1908.)

The term "bombshell" ore is applied by miners and iron-masters to hollow masses of limonite—brown hematite—which sometimes are round or oval but more commonly are of any irregular shape. "bombs" may contain water, clay, sand, quartz, flint, pyrite, siderite, sandstone or decomposed slate, or may be entirely empty. Geologists usually speak of such ore as nodular or concretionary. careful examination of the literature of ore deposits and especially of that relating to the genesis of limonite ores fails to disclose a satisfactory explanation of its origin of mode of formation. many it is assumed to be similar in origin to silicious geodes, which are supposed to be formed by the deposition of silica or silicates upon the walls of cavities, while others describe it as of "concretionary" origin without attempting to explain the process of formation or the manner in which it has occluded the variety of materials which are found in the interior of different specimens from the same locality. That it is not of concretionary origin is evident upon even cursory consideration, for concretions are masses of material arranged in concentric layers around a central nucleus. The latter may be a grain of sand, a pebble, fossil, or any substance around which (as a core) the concretion forms, growing from the center by the successive addition of concentric rings. Concretions are perhaps merely symmetrical segregations.

The peculiarities of this ore are well described by Professor T. C. Hopkins, *Bull. Geol. Soc. Am.*, 1890, Vol. 11, p. 477, etc., as follows:

"Nodular ore consists of irregularly rounded masses, varying in size from a fraction of a pound to several hundred pounds in weight. The masses are frequently hollow, but some enclose a rounded or sub-angular rock fragment, which is sometimes sandstone, . . . sometimes chert, sometimes slate, and sometimes clay. Some shells are filled with clay and sand.

and workmen report finding many of them filled with water. filled with clay, which still retains the laminated structure and appearance of the original slate from which the clay was derived, furthermore, the slaty structure was found to extend through the ore shell, which showed, besides the plain lamination of slate, a faint concentric structure as well. ... While only one shell was found still retaining the laminations of the clay, there were many others containing clay and sand. Some of the shells were but thin crusts, while others were quite thick, almost solid; some have a smooth, velvety or bright mammillated inner surface, frequently coated with manganese oxide. In some instances the lining of the shell is covered with many small stalactites of ore. . . . Many of the shells are lined with a dense fibrous layer, often an inch or more in thickness. . . . The thinner shells have all been broken, and we see only the fragments of them in the clay-ore masses. This shell form of ore . . . forms an appreciable part of the ore body in many cases. The small, irregular, nodular-like pieces of ore, commonly knows as shot ore, are presumably closely related in origin to the shells. . . ."

The inner wall of many bombs consists of a hard, bright, brown or jet-black, glazed surface, curved, rounded or botryoidal. This is frequently described as a manganese coating, but is doubtless a film of iron or manganese silicate. Occasionally the interior or a part of the interior is lined with a layer of extremely hard, flinty, liver-colored iron silicate, or with quartz crystals or chalcedony, and the same silicate frequently forms a considerable portion of the body of the shell or of its outer layers, but generally the shell is composed of high-grade limonite, of a fibrous structure, especially in those layers forming the inner lining of the shell.

These peculiarities are satisfactorily accounted for neither by the theory that these ore masses owe their origin to concretionary action, nor by that which assumes the direct deposition of ferric hydrate upon the interior of rock (limestone?) cavities. They may, however, be explained by assuming that the bombs are the residual masses, remaining after oxidation, of iron sulphides or carbonates containing sand or clay or both in varying proportions.

If the material from which this ore is formed consists of sandstone, or of sandy slate, or of clay slate, impregnated more or less completely with pyrite or siderite, the formation of bombshells, containing just such materials as are found in these shells, may be readily explained, especially if the iron impregnation be in the form of pyrite or marcasite, that is, FeS₂. If such sandstone or slate, is broken and fissured by faulting and crushing, and by the development of cleavage planes, oxidation by percolating waters will proceed along the joints or planes which form the channels through which these waters circulate, and in each fragment of the mineralized rock oxidation will commence upon the outside and progress towards the center.

In this way on outer skin or shell of limonite first forms on the outside of the fragment, for if the iron be present as pyrite or marcasite while some of it may be removed as ferrous sulphate, this salt, if formed, may immediately be oxidized and precipitated in situ as ferric hydrate. The sulphuric acid formed by the oxidation of the remaining molecule of sulphur will attack and decompose the clay of the gangue, removing the bases as sulphates in solution; the silicic acid also escaping in solution, or combining with iron oxides to form iron silicates, remains as an integral part of the ore.

If clay be present in large quantity a portion will remain undecomposed in the center of the bomb, together with all of the sand originally present in the gangue.

Hence, if the original pyritic material has a clayey (slate) gangue, bombs may form containing no residual matter, or containing more or less clay; if the gangue be sand and clay (arenaceous slate), the sand only, or sand and clay may remain; if the gangue be sand only, some of this will remain as an impurity in the limonite forming the body of the shell, and some as a partial filling of the interior of the bomb.

It is now well known that pyrite (or marcasite) oxidizing underground, whether by waters carrying free oxygen, or by waters containing no uncombined oxygen, or by reactions involving hydrolysis, does not behave in the same way as when oxidized by exposure to the air above-ground. One of the most common reactions above-ground is that in which sulphur is set free, often written:

$$FeS_2 + 4O = FeSO_4 + S$$
,

but this rarely occurs beneath the surface, for the gossans of pyritic veins seldom carry free sulphur, although there are a few noted examples in which large deposits of sulphur are found between the surface and the unoxidized portions of such veins.

In the absence of oxygen, carbonates in solution may, as shown by Dr. N. H. Stokes, completely oxidize the iron of pyrite or marcasite thus:

$$8\text{FeS}_2 + 15\text{Na}_2\text{CO}_3 = 4\text{Fe}_2\text{O}_3 + 14\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 15\text{CO}_2$$

and under proper conditions of temperature and pressure the ferric oxide thus formed may be deposited as hydrate; but these reactions do not satisfy the observed conditions and it seems more probable that oxidation near the surface has proceeded as indicated by some of the following reactions:

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\begin{split} &\operatorname{FeS}_2 + \operatorname{H}_2\operatorname{O} + 7\operatorname{O} = \operatorname{FeSO}_4 + \operatorname{H}_2\operatorname{SO}_4; \\ &\operatorname{3FeS}_2 + \operatorname{8H}_2\operatorname{O} + 2\operatorname{2O} = \operatorname{Fe}_2\operatorname{O}_3, \  \, \operatorname{3H}_2\operatorname{O} + \operatorname{FeSO}_4 + \operatorname{5H}_2\operatorname{SO}_4; \\ &\operatorname{2FeSO}_4 + \operatorname{5H}_2\operatorname{O} + \operatorname{O} = \operatorname{Fe}_2\operatorname{O}_3, \  \, \operatorname{3H}_2\operatorname{O} + \operatorname{2H}_2\operatorname{SO}_4; \\ &\operatorname{2FeS}_2 + 7\operatorname{H}_2\operatorname{O} + \operatorname{I5O} = \operatorname{Fe}_2\operatorname{O}_3, \  \, \operatorname{3H}_2\operatorname{O} + \operatorname{4H}_2\operatorname{SO}_4; \\ &\operatorname{2FeS}_2 + \operatorname{4H}_2\operatorname{O} + \operatorname{I5O} = \operatorname{Fe}_2\operatorname{O}_3 + \operatorname{4H}_2\operatorname{SO}_4; \\ &\operatorname{2FeSO}_4 + \operatorname{2H}_2\operatorname{O} + \operatorname{O} = \operatorname{Fe}_2\operatorname{O}_3 + \operatorname{2H}_2\operatorname{SO}_4; \\ &\operatorname{6FeSO}_4 + \operatorname{3O} = \operatorname{Fe}_2\operatorname{O}_3 + \operatorname{2Fe}_2(\operatorname{SO}_4)_3; \\ &\operatorname{6FeSO}_4 + \operatorname{3H}_2\operatorname{O} + \operatorname{3O} = \operatorname{Fe}_2\operatorname{O}_3, \  \, \operatorname{3H}_2\operatorname{O} + \operatorname{2Fe}_2(\operatorname{SO}_4)_3; \\ &\operatorname{2Fe}_2(\operatorname{SO}_4)_3 + \operatorname{2FeS}_2 + \operatorname{4H}_2\operatorname{O} + \operatorname{I2O} = \operatorname{6FeSO}_4 + \operatorname{4H}_2\operatorname{SO}_4. \end{split}
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The sulphuric acid having been formed in direct contact with the gangue, it is reasonable to suppose that it must at once attack any clay or other decomposable material, and the removal of the soluble silicates and silicic acid by transfusion through the walls of the bomb is readily pictured. It is, however, possible that the colloidal silicic acid may be retained, and further that it may perhaps often be set free in a gelatinous condition. This latter hypothesis may account for the frequent presence in such ores of a skeleton of amorphous silica which appears to completely ramify some parts of the limonite.

If the oxidation proceed according to these equations, the successive additions of layers of limonite to the interior of the shells is doubtless due to the further oxidation of the ferrous sulphate as above shown, the oxidation of the solution occurring at or in the wall of the shell where the solutions, in escaping by transfusion through the walls of the shell, are met by oxidizing waters transfusing towards the center of the shell. Under such conditions the ferric

hydrate would be deposited in the pores of the shell or upon its inner surface.

In attempting to picture these reactions and their results, it is important to remember the extremely slow rate at which oxidation proceeds under such conditions. Even at the surface where decomposition is comparatively rapid, the oxidation of pyrite appears to progress at a very slow rate, perhaps not exceeding an inch or a few inches in depth in several hundred years.

If the iron be present as carbonate, a precisely similar series of reactions may be conceived, in which carbonic acid transposes the silicates, freeing silicic acid and removing the bases as soluble carbonates.

Other observers have noted the occasional presence of a central core of siderite or pyrite in bombshell ore, but have generally attributed the presence of such cores to concretionary action and replacement by sulphates (accompanied by reduction to sulphide) or carbonates in solution.

The foregoing theory, advanced to account for the origin of bombshell ore, is based upon a study of these deposits dating back to 1885—when the writer was personally engaged in mining brown-hematite ore—and upon examinations of many specimens which show more or less clearly the character of the original material from which such ore is formed. It will form an integral part of a broader statement, extending the application of this theory to the genesis of limonite ores, and including a discussion of the original sources of the iron, methods of mineralization, and subsequent decomposition and precipitation.